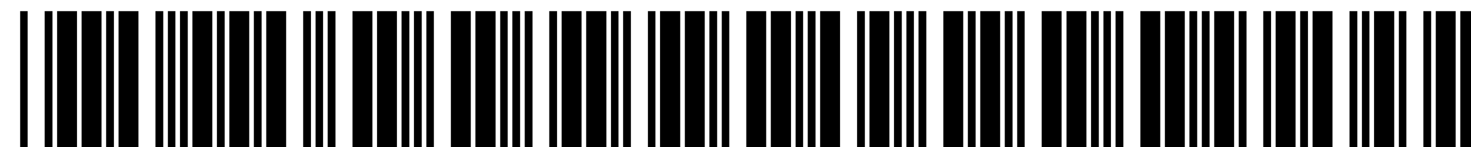

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(54) **THERMAL METHODS FOR CLEANING POST-CMP WAFERS**

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H01L 21/24 (2006.01)
H01L 21/40 (2006.01)
H01L 21/31 (2006.01)
H01L 21/469 (2006.01)

(52) **U.S. Cl.** **438/771**; 438/540; 257/E21.284

(58) **Field of Classification Search** 438/540, 438/771; 257/E21.284
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,773,132 A * 6/1998 Blumberg et al. 428/209
6,127,282 A 10/2000 Lopatin
6,717,189 B2 4/2004 Inoue et al.
6,878,628 B2 4/2005 Sophie et al.
6,902,605 B2 6/2005 Kolics et al.
2001/0053591 A1* 12/2001 Buchwalter et al. 438/584
2003/0157774 A1* 8/2003 Tominari et al. 438/312
2005/0158999 A1* 7/2005 Lin et al. 438/687

FOREIGN PATENT DOCUMENTS

KR 10-2001-0089722 10/2001
KR 10-2002-0025806 4/2002

OTHER PUBLICATIONS

International Application Serial No. PCT/US2008/005744, International Search Report and Written Opinion mailed Oct. 24, 2008, 9 pgs.

(Continued)

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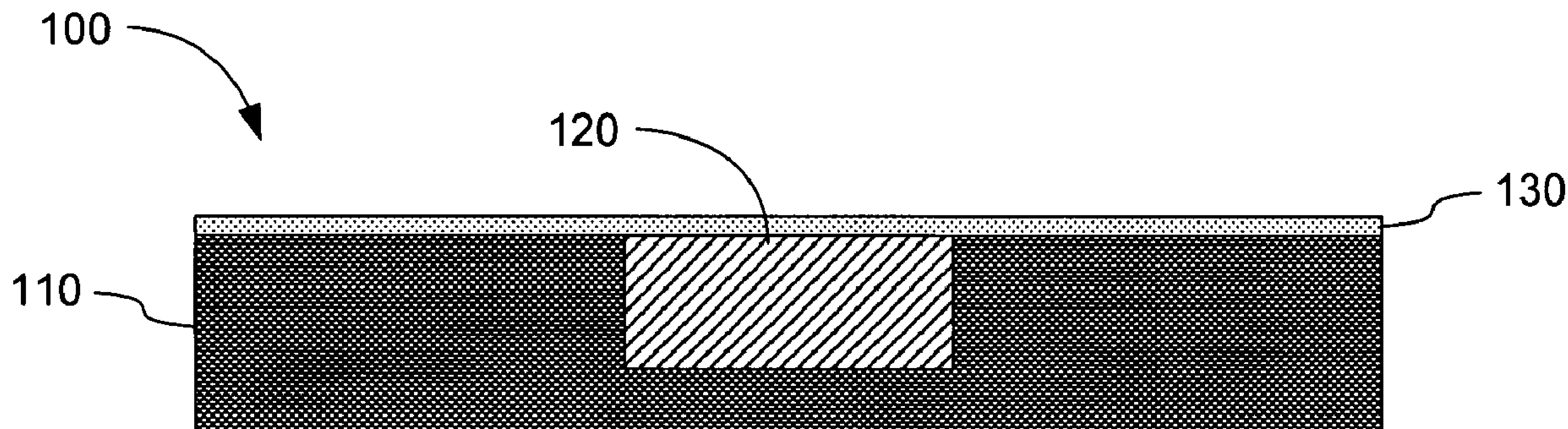
(57) **ABSTRACT**

Methods for cleaning semiconductor wafers following chemical mechanical polishing are provided. An exemplary method exposes a wafer to a thermal treatment in an oxidizing environment followed by a thermal treatment in a reducing environment. The thermal treatment in the oxidizing environment both removes residues and oxidizes exposed copper surfaces to form a cupric oxide layer. The thermal treatment in the reducing environment then reduces the cupric oxide to elemental copper. This leaves the exposed copper clean and in condition for further processing, such as electroless plating.

25 Claims, 3 Drawing Sheets



OTHER PUBLICATIONS

Christensen, T. M. et al., "Thermal Stability of Benzotriazole on Copper during Atmospheric Corrosion", Surface and Interface Analysis, vol. 17, 3-6 (1991).

Kirsch, P. D. et al., "Chemical and thermal reduction of thin films of copper (II) oxide and copper (I) oxide", Jrnl. of Applied Physics, vol. 90, No. 8, Oct. 15, 2001, pp. 4256-4264.

Kim, J. Y., et al., "Reduction of CuO and Cu2O with H2: H Embedding and Kinetic Effects in the Formation of Suboxides", J. Am. Chem. Soc. 2003, 125, 10684-10692.

Hymes, S., et al., "Surface cleaning of copper by thermal and plasma treatment in reducing and inert ambients", J. Vac. Sci. Technol. B 16(3), May/Jun. 1998, pp. 1107-1109.

* cited by examiner

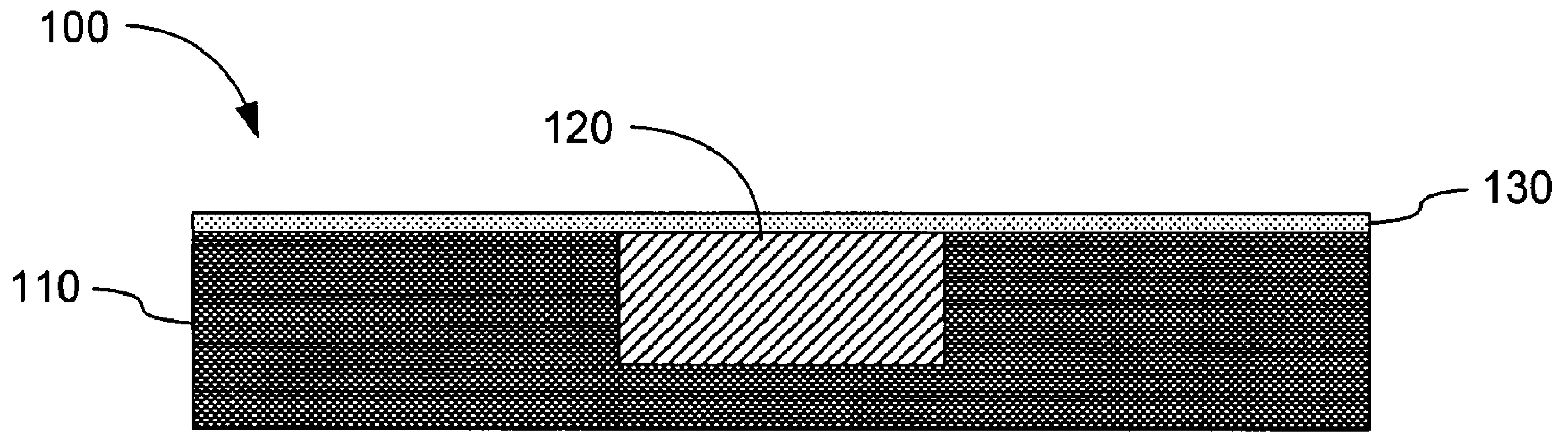


FIG. 1

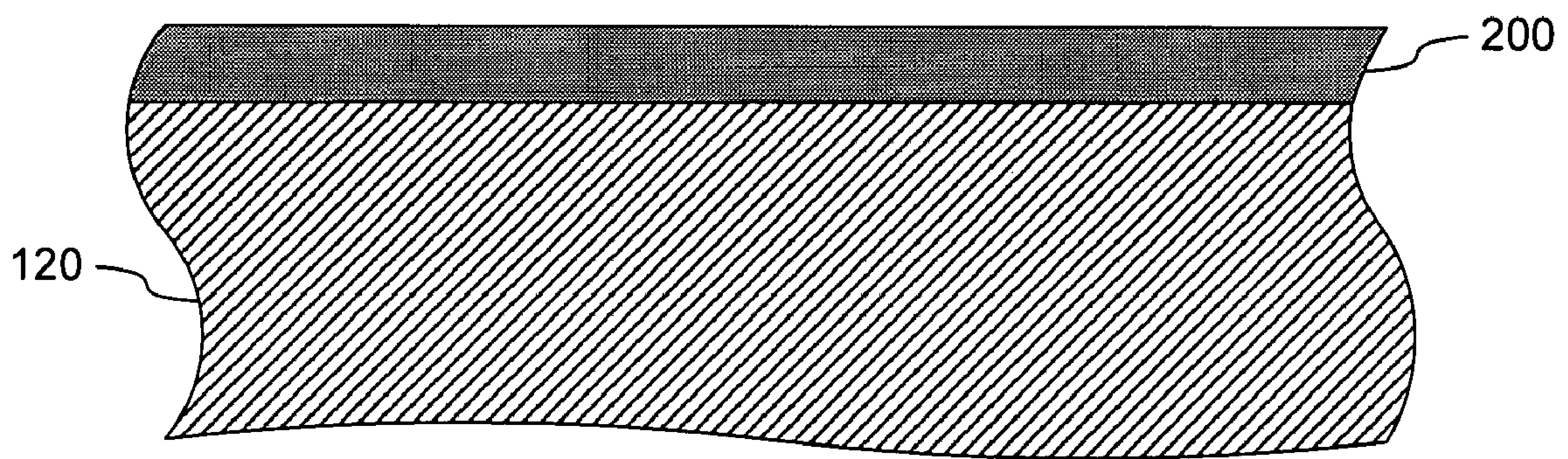


FIG. 2

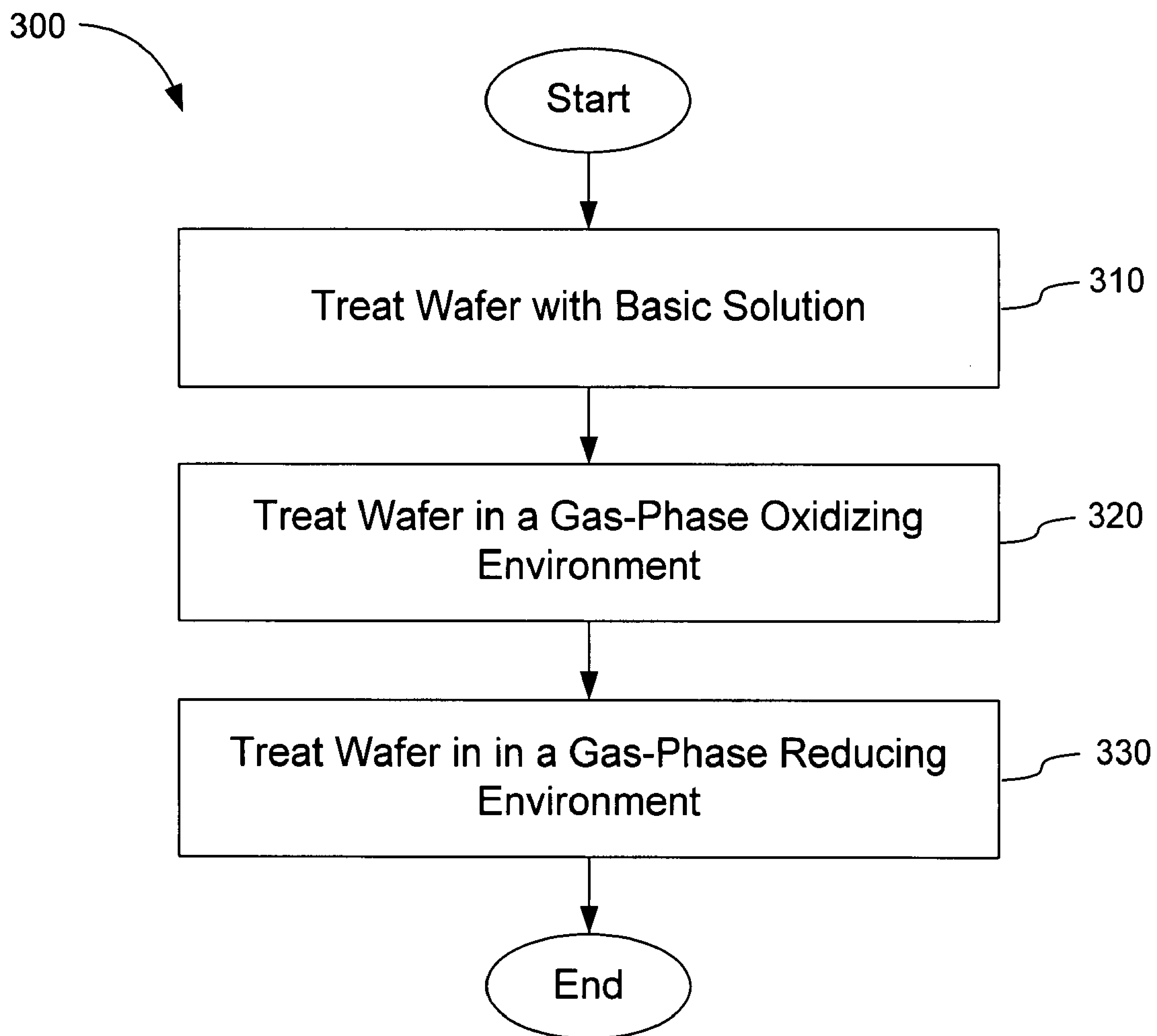


FIG. 3

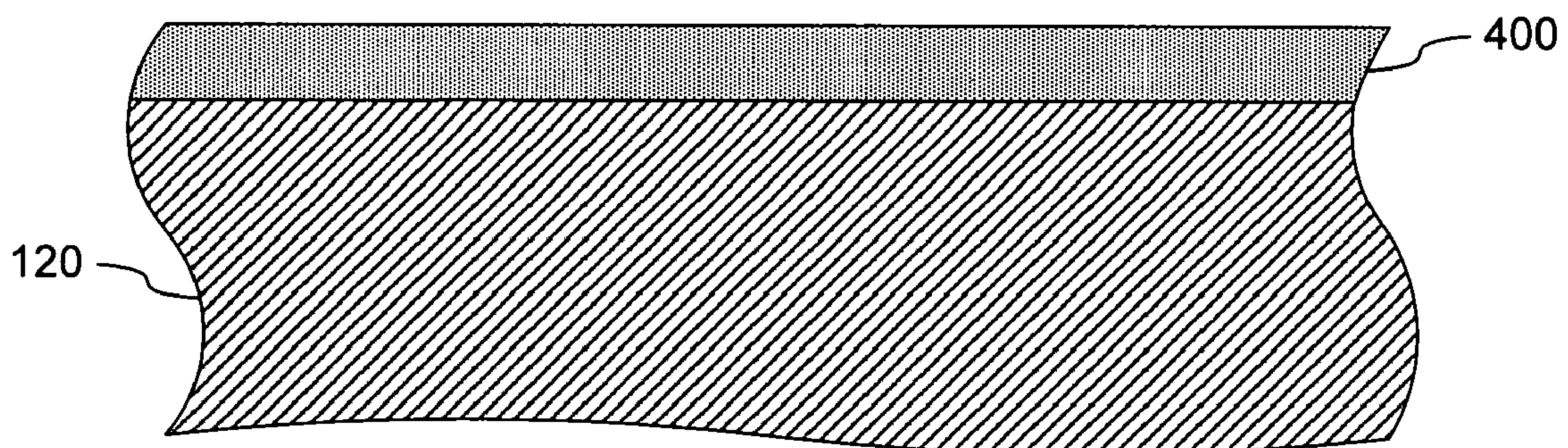


FIG. 4

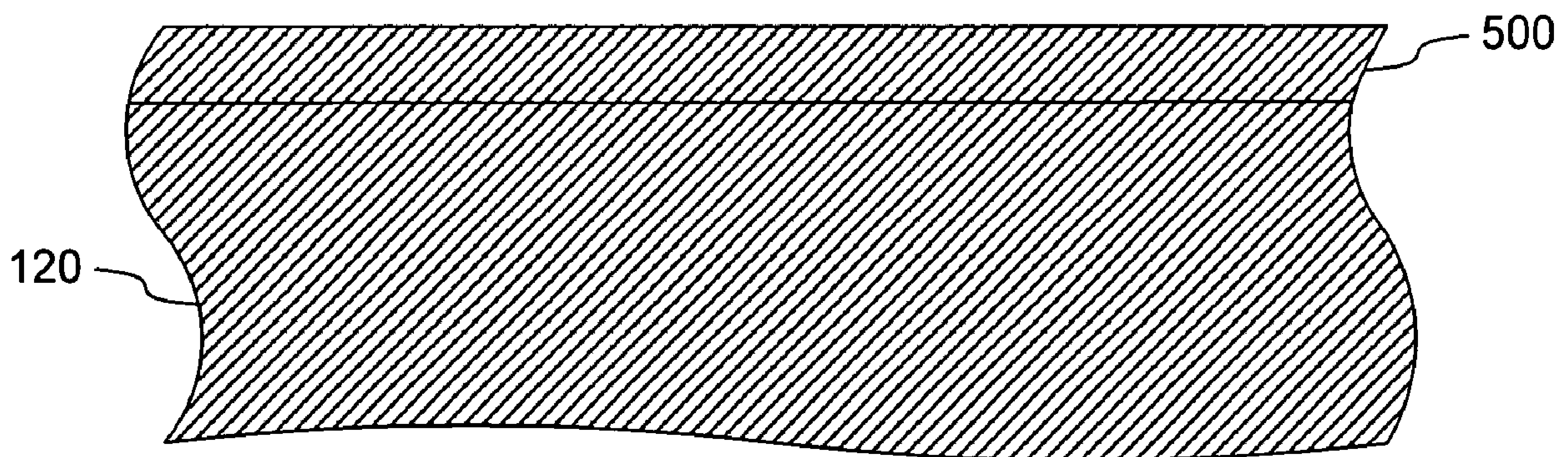


FIG. 5

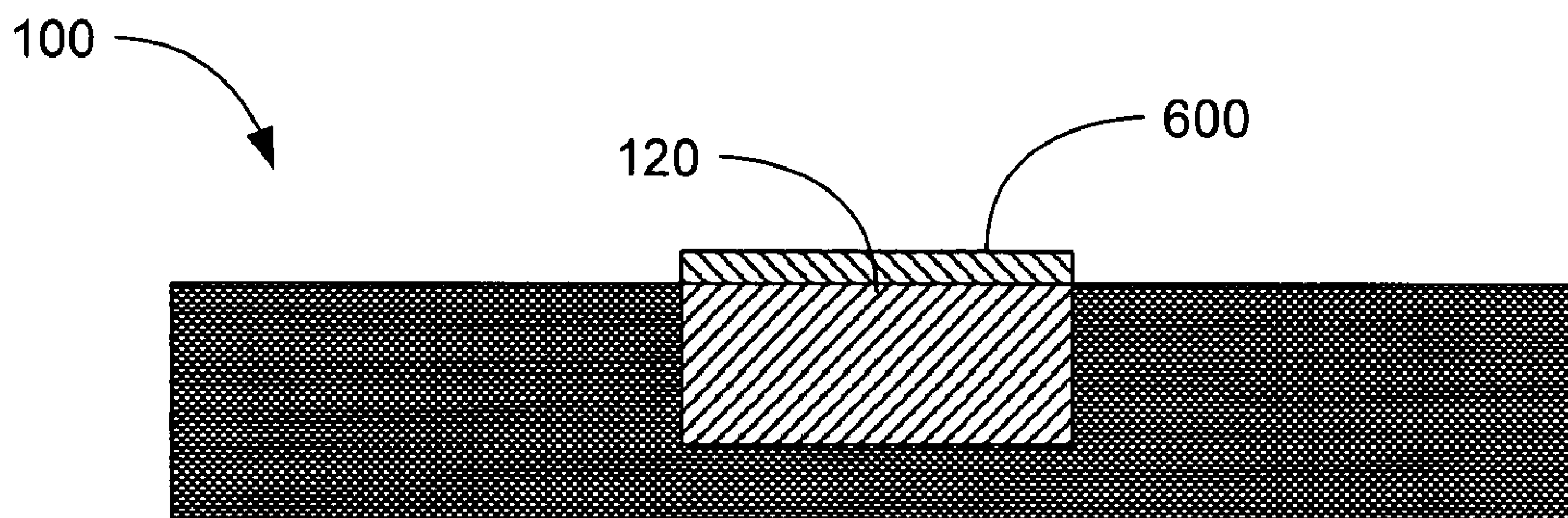


FIG. 6

THERMAL METHODS FOR CLEANING POST-CMP WAFERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to the field of semiconductor device fabrication and more particularly to wafer cleaning.

2. Description of the Prior Art

Semiconductor devices, including the Back-End of Line (BEoL) interconnect structures thereof, include conductive lines and other features that are formed from copper. During semiconductor device fabrication on a wafer, the copper is typically deposited within trenches or vias defined in a dielectric layer. The copper and dielectric layers are then planarized to provide a smooth and planar surface on which to deposit additional layers. A common method for planarizing is chemical mechanical planarization (CMP). CMP processes typically leave a residue on the exposed surface of the wafer that must be removed prior to the formation of subsequent layers.

Typical approaches to removing the CMP residue involve washing the wafer. For example, the wafer can be washed first in an acidic solution and then in a basic solution, or first in a basic solution followed by an acidic solution. However, these methods are disadvantageous as they tend to remove copper, leaving the copper features recessed with respect to the surrounding dielectric layer. Other methods for removing the CMP residue expose the wafer to an energetic plasma to etch away the residue.

What is provided by the present invention are novel methods for removing CMP residue that do not harm either the exposed copper or the dielectric layer.

SUMMARY

An exemplary post-CMP cleaning method comprises treating a wafer in a gas-phase oxidizing environment at a temperature above about 100° C., then treating the wafer in a gas-phase reducing environment at a temperature above about 100° C. Treating the wafer in the oxidizing environment can include treating the wafer in an atmosphere comprising O_2 or O_3 while treating the wafer in the reducing environment can include treating the wafer in an atmosphere comprising H_2. The method can further comprise treating the wafer with a basic solution prior to treating the wafer in the oxidizing environment. The basic solution can have a pH in the range of about 8 to about 11, for example, and in some embodiments comprises tetramethyl ammonium hydroxide.

The present invention also provides a method for cleaning a post-CMP wafer that includes a conductive feature having a Cu_2O surface layer. This exemplary method comprises oxidizing the Cu_2O surface layer in a first gas-phase environment to form a CuO surface layer, then reducing the CuO surface layer in a second gas-phase environment to elemental Cu. Oxidizing the Cu_2O surface layer can comprise treating the wafer in an atmosphere including O_2 or O_3 at a temperature above about 100° C., while reducing the CuO surface layer can comprise treating the wafer in an atmosphere including H_2 at a temperature above about 100° C. The method can further comprise substantially removing a residue layer with a basic solution prior to oxidizing the Cu_2O surface layer.

Another method of the invention is directed to selectively forming a capping layer over a conductive feature of a wafer. This exemplary method comprises cleaning the wafer and forming the capping layer selectively over the conductive feature by electroless deposition. In this method, cleaning the wafer can include oxidizing a Cu_2O surface layer of the conductive feature in a first gas-phase environment to form a CuO surface layer, then reducing the CuO surface layer in a second gas-phase environment to elemental Cu. In some embodiments, the capping layer comprises cobalt or a cobalt alloy.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is a cross-section view of a post-CMP wafer including a conductive feature disposed within a dielectric layer.

FIG. **2** is a cross-section view of the top portion of the conductive feature of FIG. **1**.

FIG. **3** is a flow-chart representation of a method for cleaning the post-CMP wafer of FIG. **1** according to an embodiment of the present invention.

FIG. **4** is a cross-section view of the top portion of the conductive feature shown in FIG. **2** following treatment in an oxidizing environment according to an embodiment of the present invention.

FIG. **5** is a cross-section view of the top portion of the conductive feature shown in FIG. **3** following treatment in a reducing environment according to an embodiment of the present invention.

FIG. **6** is a cross-section view of a wafer including a capping layer selectively disposed on a conductive feature according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides methods for cleaning semiconductor wafers following chemical mechanical polishing. An exemplary method exposes a wafer to a thermal treatment in an oxidizing environment followed by a thermal treatment in a reducing environment. The thermal treatment in the oxidizing environment both removes residues and oxidizes exposed copper surfaces to form a cupric oxide layer. The thermal treatment in the reducing environment then reduces the cupric oxide to elemental copper. This leaves the exposed copper clean and in condition for further processing, such as electroless plating.

FIG. **1** is a cross-sectional view of a wafer **100** following a chemical mechanical polishing (CMP) process. The wafer **100** comprises a dielectric layer **110** and an exposed conductive feature **120** disposed within the dielectric layer **110**. FIG. **1** also shows a residue layer **130** left by the CMP process on the surfaces of the dielectric layer **110** and the conductive feature **120**. The residue layer **130** can include, for example, cleaning residues and corrosion inhibitors, which are typically copper-organic complexes. The residue layer **130** should be removed as completely as possible prior to further processing, such as electroless deposition on the conductive feature **120**.

The dielectric layer **110** can comprise SiO_2 or a low dielectric constant ("low-k") material that has a dielectric constant less than that of SiO_2. Such low-k materials, especially those with dielectric constants lower than 3, are increasingly favored in semiconductor device fabrication as they impart superior electrical properties to the finished devices. Examples of suitable low-k materials include fluorosilicate glass (FSG), organosilicate glass (OSG), and highly porous SiO_2.

The conductive feature **120** can be a conductive line or via made of copper, for example. Although only one conductive feature **120** is shown in FIG. **1**, the conductive feature **120** is

used to represent the large number of conductive features that are typically present on a wafer **100**.

FIG. **2** shows an enlarged view of a top portion of the conductive feature **120** in FIG. **1**. The residue layer **130** has been omitted from FIG. **2** for clarity. As shown in FIG. **2**, when the conductive feature **120** comprises copper, the CMP process leaves the conductive feature **120** with a thin surface layer **200** of cuprous oxide (Cu_2O).

FIG. **3** is a flow-chart representation of an exemplary method **300** for cleaning the wafer **100** to remove the residue layer **130**. The method comprises optionally treating **310** the wafer **100** with a basic solution, treating **320** the wafer in a gas-phase oxidizing environment, and treating **330** the wafer in a gas-phase reducing environment. Here, "gas-phase" indicates that the phase of matter within the environment is a gas, as opposed to a plasma.

The method **300** optionally begins by treating **310** the wafer **100** with a basic solution. In some embodiments, the basic solution has a pH of 10; a suitable pH range for the basic solution is about 8 to about 11. An exemplary basic solution comprises tetramethyl ammonium hydroxide. A suitable dwell time in the basic solution under these conditions is about 30 seconds to about 2 minutes. Treating **310** the wafer **100** with the basic solution serves to remove a substantial portion of the residue layer **130** from the surface of the dielectric layer **110** and the surface of the conductive feature **120**. In some embodiments, the treatment **310** leaves approximately a monolayer of the residue layer **130** on both the surface of the dielectric layer **110** and the surface of the conductive feature **120**. Treating **310** with the basic solution does not meaningfully alter the Cu_2O surface layer **200** (FIG. **2**).

Next, the wafer **100** is treated **320** in an oxidizing environment. As treating **310** the wafer **100** with the basic solution is optional, in some embodiments the method **300** begins with treating **320** in the oxidizing environment. An exemplary oxidizing environment comprises an atmosphere including about 1% to about 10% molecular oxygen (O_2), or about 1% to about 2% ozone (O_3), with the balance of the atmosphere being an inert gas such as nitrogen, helium, or argon. All percentages used herein are volume percents unless noted otherwise.

A suitable temperature range for the oxidizing environment is about 100° C. to about 400° C. A more preferable temperature is in the range of about 150° C. to about 250° C. The pressure within the oxidizing environment can be at or below normal atmospheric pressure. An exemplary pressure is about 1 Torr. A suitable dwell time in the oxidizing environment under these conditions is about 2 minutes, but can be in the range of about 1 minute to about 5 minutes. Omitting the optional treating **310** the wafer **100** with the basic solution generally results in longer dwell times.

Treating **320** in the oxidizing environment serves to decompose and volatilize the organic materials in the residue layer **130**. The elevated temperature of the oxidizing environment also serves to desorb water in the residue layer **130**. Additionally, the oxidizing environment serves to oxidize the Cu_2O surface layer **200** of the conductive feature **120**. As shown in FIG. **4**, the Cu_2O surface layer **200** (FIG. **2**) is oxidized to form a cupric oxide (CuO) surface layer **400**.

Next, the wafer **100** is treated **330** in a reducing environment. An exemplary reducing environment comprises an atmosphere including molecular hydrogen (H_2). The atmosphere can be essentially entirely hydrogen, or can comprise a mixture of hydrogen with an inert gas such as nitrogen, helium, or argon. The pressure within the reducing environment can be at or below normal atmospheric pressure. At normal atmospheric pressure, a suitable concentration of hydrogen is about 4%. At lower pressures, such as in the range of about 1 Torr to about 10 Torr, the atmosphere can be entirely hydrogen. A suitable temperature range for the reducing environment is about 100° C. to about 400° C. A more preferable temperature is in the range of about 150° C. to about 250° C. In some embodiments, the same temperature is maintained through both treatments **320** and **330**. A suitable dwell time in the reducing environment under these conditions is about 1 minute to about 2 minutes.

As shown in FIG. **5**, treating **330** in the reducing environment serves to reduce the CuO surface layer **400** (FIG. **4**) to a surface layer **500** of elemental copper (Cu). Following treating **330** in the reducing environment, the wafer **100** can be further processed, for example, by selective electroless plating of a capping layer on the conductive feature **120**. Methods for electroless plating of cobalt and cobalt alloys are taught, for example in U.S. patent application Ser. No. 11/644,697 filed on Dec. 22, 2006 and entitled "Electroless Deposition of Cobalt Alloys," and U.S. patent application Ser. No. 11/513,634 filed on Aug. 30, 2006 and entitled "Processes and Systems for Engineering a Copper Surface for Selective Metal Deposition" each of which is incorporated herein by reference. FIG. **6** shows the wafer **100** after a capping layer **600** has been selectively formed on the conductive feature **120** by electroless plating. Advantageously, the elemental copper surface layer **500** provides a superior surface for the nucleation and growth of cobalt and cobalt alloy capping layers than the Cu_2O surface layer **200**.

In the foregoing specification, the invention is described with reference to specific embodiments thereof, but those skilled in the art will recognize that the invention is not limited thereto. Various features and aspects of the above-described invention may be used individually or jointly. Further, the invention can be utilized in any number of environments and applications beyond those described herein without departing from the broader spirit and scope of the specification. The specification and drawings are, accordingly, to be regarded as illustrative rather than restrictive.

What is claimed is:

1. A post-CMP cleaning method comprising:

treating a wafer in a gas-phase oxidizing environment at a temperature above about 100° C.; then

treating the wafer in a gas-phase reducing environment at a temperature above about 100° C.

2. The method of claim **1** wherein treating the wafer in the oxidizing environment includes treating the wafer in an atmosphere comprising O_2.

3. The method of claim **2** wherein the atmosphere comprises between about 1% to about 10% O_2.

4. The method of claim **1** wherein treating the wafer in the oxidizing environment includes treating the wafer in an atmosphere comprising O_3.

5. The method of claim **4** wherein the atmosphere comprises between about 1% to about 2% O_3.

6. The method of claim **1** wherein the temperature of the oxidizing environment is between about 150° C. to about 250° C.

7. The method of claim **1** wherein a pressure within the oxidizing environment is about 1 Torr.

8. The method of claim **1** wherein treating the wafer in the oxidizing environment includes holding the wafer in the oxidizing environment for a dwell time of between about 1 minute to about 5 minutes.

9. The method of claim **1** wherein treating the wafer in the reducing environment includes treating the wafer in an atmosphere comprising H_2.

10. The method of claim **9** wherein the atmosphere comprises a mixture of H_2 and an inert gas.

11. The method of claim **1** wherein a pressure within the reducing environment is between about 1 Torr to about 10 Torr.

12. The method of claim **1** wherein the temperature of the reducing environment is between about 150° C. to about 250° C.

13. The method of claim **1** wherein a temperature of the oxidizing environment and a temperature reducing environment are the same.

14. The method of claim **1** wherein treating the wafer in the reducing environment includes holding the wafer in the reducing environment for a dwell time of between about 1 minute to about 2 minutes.

15. The method of claim **1** further comprising treating the wafer with a basic solution prior to treating the wafer in the oxidizing environment.

16. The method of claim **15** wherein the basic solution has a pH in the range of about 8 to about 11.

17. The method of claim **15** wherein the basic solution comprises tetramethyl ammonium hydroxide.

18. The method of claim **15** wherein treating the wafer in the basic solution includes holding the wafer in the basic solution for a dwell time of between about 30 seconds to about 2 minutes.

19. A method for cleaning a post-CMP wafer including a conductive feature having a Cu_2O surface layer, the method comprising:

oxidizing the Cu_2O surface layer in a first gas-phase environment to form a CuO surface layer; then

reducing the CuO surface layer in a second gas-phase environment to elemental Cu.

20. The method of claim **19** wherein the first gas-phase environment comprises an atmosphere including O_2 at a temperature above about 100° C.

21. The method of claim **19** wherein the first gas-phase environment comprises an atmosphere including O_3 at a temperature above about 100° C.

22. The method of claim **19** wherein the second gas-phase environment comprises an atmosphere including H_2 at a temperature above about 100° C.

23. The method of claim **19** further comprising substantially removing a residue layer with a basic solution prior to oxidizing the Cu_2O surface layer.

24. The method of claim **23** wherein the basic solution has a pH in the range of about 8 to about 11.

25. The method of claim **23** wherein the basic solution comprises tetramethyl ammonium hydroxide.

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